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13. ABSTRACT (Maximum 200 words)

The objectives of this research program were to synthesize and characterize nanostructured thermal spraying coatings including: (1) Synthesis of nanostructured powders for fabrication of nanostructured thermal spraying coatings; (2) Development of the spray technology for spraying nanostructured powders; and (3) Characterization of the nanostructured materials-powder as well as coatings—for structure, composition, properties and performance. Under this program, the following accomplishments have been achieved: (1) Successful synthesis of diverse nanostructured feedstock powders using mechanical milling in different media. Chemical composition and structural analyses were performed for the powders milled for a pre-determined interval, so that the milling process and behavior of resultant powder was monitored and optimized; (2) Thermal spraying for nanostructured coatings with improved performance, i.e. an increase of 20 % in hardness and 28% in wear resistance in nanostructured Cr_3C_2-NiCr coatings have been accomplished. Nanostructured powders were thermally sprayed, as well as conventional ones for comparison purpose using an HVOF facility equipped with in-flight powder diagnostics system. Combined with modeling results, behavior of powders during spraying was investigated; (3) Characterization of the nanostructured coatings has been performed using microhardness, Nanoidentor, SEM, X-ray diffraction, and TEM, so that hardness, wear-resistance, and microstructures were investigated. On the basis of the feedback of the physical properties of the coatings, the spraying parameters were modified and optimum spraying conditions were reached for an individual nanostructured powder, i.e. techniques for synthesizing nanostructured WC-18Co coatings containing low amount of non-WC carbide phases were developed; and (4) Development of thermal treatment techniques to further improve physical performance of nanostructured coatings, i.e. post-heat treatment can cause significant increase in hardness and scratch resistance of the nanostructured Cr_3C_2-NiCr coatings.

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1. List of Publications

Journal Articles:

1. H. G. Jiang, M. Rühle and E.J. Lavernia, "On the applicability of the X-ray diffraction line profile analysis in extracting grain size and microstrain in nanocrystalline materials", *Journal of Materials Research,* Vol. 14, No. 2, pp. 549-559, 1999.
2. H.G. Jiang, R.J. Perez, M.L. Lau and E.J. Lavernia, "Formation kinetics of nanocrystalline Fe-4 wt. % Al solid solution during ball milling", *Journal of Materials Research,* Vol. 12, No. 6, pp. 1429-1432, 1997.
3. R.J. Perez, H.G. Jiang, C.P. Dogan and E.J. Lavernia, "Grain growth of nanocrystalline cryomilled Fe-AL powders", *Metallurgical and Materials Transactions A,* Vol. 29A, pp. 2469-2475, 1998.
4. M.L. Lau, H.G. Jiang, W. Nuchter,and E.J. Lavernia, "Thermal spraying of nanocrystalline Ni coatings", *Solidi Status Physica,* pp. 257-268, 1998.
5. B. Huang, R.J. Perez, H. Hu and E.J. Lavernia, "Grain growth of nanocrystalline Fe-Al alloys produced by cryomilling in liquid argon and nitrogen", *Materials Science and Engineering A* 255, pp. 124-132, 1998.
6. M.L. Lau, E. Strock, A. Fabel, C.J. Lavernia and E.J. Lavernia, "Synthesis and characterization of nanocrystalline Co-Cr coatings by plasma spraying", *NanoStructured Materials,* Vol. 10, No.5, pp. 723-730, 1998.
7. J. He, M. Ice and E.J. Lavernia, "Synthesis and characterization of nanostructured Cr_3C_2-NiCr", *NanoStructured Materials,* Vol. 10, No. 8, pp.1271-1283, 1998.
8. H.G. Jiang, H.M. Hu and E.J. Lavernia, "Synthesis of Fe rich Fe-Al nanocrystalline solid solutions using ball milling", *Journal of Materials Research,* Vol. 14, No. 5, pp. 1760-1770, 1999.
9. M.L. Lau and E.J. Lavernia, "Microstructural evolution and oxidation behavior of nanocrystalline 316-stainless steel coatings produced by high velocity oxygen-fuel spraying", *Materials Science & Engineering A Special Issue - Herb Herman "Festschrift"*, A 272, pp. 222-229, 1999.
10. R. Hayes, V. Tellkamp and E.J. Lavernia, "A preliminary creep study of a bulk nanocrystalline Al-Mg alloy", *Scripta Materialia,* Vol. 41, No. 7, pp. 743-748, 1999.
11. M.L. Lau, V.V. Gupta and E.J. Lavernia, "Particle behavior of nanocrystalline 316-stainless steel during high velocity oxy-fuel thermal spray", *NanoStructured Materials,* Vol. 12, pp. 319-322, 1999.
12. V.L. Tellkamp and E.J. Lavernia, "Processing and mechanical properties of nanocrystalline 5083 Al Alloy", *NanoStructured Materials*, Vol. 12, pp. 249-252, 1999.
13. V. L. Tellkamp, M. Ice and E. J. Lavernia, "Consolidation and mechanical properties of a nanostructured 5083 Al alloy", *P/M Science & Technology Briefs,* Vol. 1, No. 2, pp. 22-25, 1999.
14. J. He, M. Ice and E.J. Lavernia, "Synthesis of nanostructured Cr3C2-25 (Ni20Cr) coatings", *Metallurgical and Materials Transactions*, Vol. 31A, pp. 555-564, 2000.
15. J. He, M. Ice and E.J. Lavernia, "Synthesis of nanostructed WC-12% Co coating using mechanical milling and HVOF thermal spraying", *Metallurgical and Materials Transactions*, Vol. 31A, pp. 541-553, 2000.
16. B. Huang, H.G. Jiang, R. Perez, S. Nutt and E.J. Lavernia, "Effects of Ni on the cryogenic attritor milling of metal glass $Fe_7B_{13}Si_9$ ", *NanoStructured Materials*, Vol. 11, No. 8, pp. 1009-1016, 1999.
17. J. He and E.J. Lavernia, "Precipitation phenomenon in nanostructured Cr3C2-NiCr coatings", *Materials Science and Engineering,* A301, pp. 69-79, 2001.
18. B.C. Moon, Z.H. Lee and E.J. Lavernia, "In-situ temperature measurement of A2 tool steel and axis symmetric thermal analysis", *Journal of Materials Research,* Vol. 15, pp. 1669-1678, 2000.
19. R.W. Hayes, V. Tellkamp, and E.J. Lavernia, "Creep behavior of a cryomilled ultrafine-grained Al-4% Mg alloy", *Journal of Materials Research*, Vol. 15, No. 10, pp. 2215-2222, 2000
20. V.L. Tellkamp, S. Dalek, D, Cheng and E.J. Lavernia, "Grain growth behavior of a nanostructured 5083 Al-Mg alloy, " *Journal of Materials Research,* Vol. 16, pp. 938-944, 2001.
21. J. He, L. Adelsztajn and E.J. Lavernia, "Thermal stability of nanocrystalline WC-Co powder synthesized using mechanical milling at low temperature", *Journal of Materials Research,* Vol. 16, pp.477-488, 2001.
22. J. He, F. Zhou, G. Chang and E.J. Lavernia, "Influence of Mechanical Milling on Microstructure of 49Fe-49Co-2V Soft Magnetic Alloy", *Journal of Materials Science,* Vol. 36, pp. 2955-2964. 2001.
23. J. He, M. Ice and E.J. Lavernia, "Particle melting behavior during HVOF thermal spraying", *Journal of Thermal Spray Technology,* Vol.10, pp. 83-89, 2001.
24. D. Cheng, Q. Xu, G. Trapaga, E.J. Lavernia, "The Effect of particle size and morphology on the in-flight behavior of particles during high velocity oxy-fuel (HVOF) thermal spraying, " *Metallurgical and Materials Transactions B,* Vol 32B, pp. 525-535, 2001.

25. D. H Shin, Y.-S. Kim and E.J. Lavernia, "Formation of fine cementite precipitates by static annealing of equal channel angular pressed low carbon steels " *Acta Materialia,* Vol. 49 , pp. 2387-2393, 2001.
26. J. He, M. Ice, J.M. Schoenung, D.H. Shin, and E.J. Lavernia, "Thermal stability of nanostructured Cr_3C_2-NiCr coatings", *Journal of Thermal Spray Technology*, Vol. 10, pp. 293-300, 2001.
27. J. He, Y. Liu, Y. Qiao, T.E. Fischer and E.J. Lavernia, "Near-nanostructured WC-18% pct Co coatings with Low amounts of non-WC carbide phase Part I: synthesis and characterization", *Metallurgical and Materials Transactions* Vol. 33A, pp. 145-157, 2002.
28. Y. Liu, Y. Qiao, J. He, E.J. Lavernia, and Traugott Fischer " Near-nanostructured WC-18% pct Co coatings with low amounts of Non-WC carbide phase Part II: hardness and resistance to sliding and abrasive wear", *Metallurgical and Materials Transactions,* Vol. 33A, pp. 159-164, 2002.
29. F.T. Parker, F.E. Spada, A.E. Berkowitz, K.S. Vecchio, E.J. Lavernia and R. Rodriguez, "Thick amorphous ferromagnetic coatings via thermal spraying of spark-eroded powder", *Materials Letters*, Vol. 48, pp. 184-187, 2001.
30. D. Cheng, V.L. Tellkamp, C.J. Lavernia, and E.J. Lavernia, "Corrosion properties of nanocrystalline Co-Cr coatings" *Annals of Biomedical Engineering,* Vol. 29, pp.803-809, 2001.
31. J. He and E.J. Lavernia, "Development of nanocrystalline structure during cryomilling of Inconel 625, " *Journal of Materials Research,*Vol. 16, pp. 2724-2732, 2001.
32. J.Lee, F. Zhou, K.H. Chung, N.J. Kim, and E.J. Lavernia, "Grain growth of nanocrystalline Ni powders prepared by cryomilling", *Metallurgical and Materials Transactions,* Vol. 32A, pp. 3109-3115, 2001.
33. L. Ajdelsztajn, J. Lee, K. Chung, F.L. Bastian and E.J. Lavernia, "Synthesis and nanoindentaion study of HVOF thermal sprayed nanocrystalline and near-nanocrystalline Ni coatings", *Metallurgical and Materials Transactions,*Vol. 33A, pp. 647-655, 2002.
34. M.L. Lau, J. He, A.J. Melmed, T.A. Lusby, R. Schweinefest, M. Rühle, and E.J. Lavernia, "Microstructural evolution in nanocrystalline Ni coatings", *Journal of Materials Research*, Vol. 17, pp. 1041-1049, 2002
35. J. He, M. Ice and E.J. Lavernia, "Synthesis and processing of nanostructured Cr3C2-NiCr coatings using mechanical milling and HVOF, " *Journal of Metastable and Nanocrystalline Materials,*Vols. 312-316, pp. 237-246, 1999.
36. M. Ice, R. Rodriguez, D. Cheng, G. Kim, M. Trudeau, J. Terlecki and E.J. Lavernia, "Synthesis and Characterization of Cryomilled SiC Reinforced Composite Coatings", *Materials Science Forum,* Vols. 343-346, pp. 267-272, 2000.
37. J. He, M. Ice and E.J. Lavernia, "Thermal stability of nanostructured Cr_3C_2-NiCr coatings", *Materials Science Forum Vols.* 343-346, pp. 261-266, 2000.
38. D. Cheng, G. Trapaga, J.W. McKelliget, E.J. Lavernia, "Mathematical modeling of high velocity oxygen fuel thermal spraying: an overview", *Modelling and Simulation, Materials Science and Engineering,* in press, 2003.
39. J. He, K. H. Chung, X. Liao, Y. T. Zhu, and E.J. Lavernia, "Mechanial milling induced deformation twinning in FCC materials with high stacking fault energy", *Metallurgical and Materials Transactions,* in press, 2003.
40. R.W. Hayes, R. Rodriguez and E.J. Lavernia, "The mechanical behavior of a cryomilled Al-10Ti-2cu alloy" *Acta Materialia,* in press, 2003.

Proceedings:

1. E.J. Lavernia, M.L. Lau, and H.G. Jiang, "Thermal spray processing of nanocrystalline materials", *Nanostructured Materials, Proceedings of the NATO Advanced Study Institute on Nanostructures Materials: Science and Technology,* G.M. Chow and N.J. Noskova, eds., pp. 283-302, 1998, August 10-20, 1997, St. Petersburg, Russia.
2. S.M. Jaffe, E.J. Lavernia, "The deposition efficiency of thermally sprayed nanopowders", *Proceedings of The United Thermal Spray Conference*, March 17-19, 1999, Dusseldorf, Germany. ONR Grants: N00014-94-1-0017 and N00014-97-1-0844
3. V. L. Tellkamp, M. Ice and E.J. Lavernia, "Consolidation and mechanical properties of nanostructured Al-alloys", *Proceedings* of *powder metallurgy aluminum & light alloys for automotive applications*, November 10-11, 1998, Dearborn, MI.
4. J. He, M. Ice and E. J. Lavernia, "Synthesis and processing of nanostructured Cr3C2-NiCr coatings using mechanical milling and HVOF", *Proceedings of ISMANAM 98*, December 7-12, 1998, Wollongong, Australia.
5. J. He, M. Ice, E.J. Lavernia, "Thermal stability of nanostructured Cr_3C_2-NiCr coatings", *Proceedings of ISMANAM-99,* August 29 - September 3, 1999, Dresden, Germany.
6. M. L. Lau, H.G. Jiang and E.J. Lavernia, "Synthesis and characterization of nanocrystalline 316-stainless steel coatings by high velocity oxy-fuel spraying", *Proceedings of 15th International Thermal Spray*, C. Coddett, ed., Vol. 1, pp. 379-384, May 25-29, 1998, Nice, France.
7. H.G. Jiang, M.L. Lau and E.J. Lavernia, "Thermal stability of nanocrystalline Inconel 718 and Ni prepared by high velocity oxy-fuel (HVOF) thermal spraying", *Proceedings of 15th International Thermal Spray* , C. Coddett, ed., Vol. 2, pp. 1265-1269, May 25-29, 1998, Nice, France.

8. J. He, M. Ice and E.J. Lavernia, "Synthesis and characterization of nanocomposite coatings", *Nanostructured Films and Coatings, Proceedings of NATO Advanced Research Workshop*, pp. 131-148, 2000, June 28-30, 1999, Santorini, Greece.
9. M. Ice, R. Rodriguez, D. Cheng, G. Kim, M. Trudeau, J. Terlecki and E.J. Lavernia, "Synthesis and characterization of cryomilled SiC reinforced composite coatings", *Proceedings of ISMANAM-99*, September 1999, Dresden, Germany 1999.
10. D. Cheng, J. He, R. Rodriguez, M. Ice, and E. J. Lavernia, "Synthesis of nanocrystalline Inconel 625 powders by cryomilling", *Proceedings of Surface Engineering in Materials Science I* (2000 TMS annual meeting), edited by S. Seal, N.B. Dahotre, J.J. Moore and B. Mishra, pp. 13-21, March 12-16, 2000, Nashville, Tennessee.
11. R. Rodriguez, Mike Ice, G. Kim and E. J. Lavernia, "Thermal Spraying of Nanocomposite Coatings", *Proceedings of 2000 TMS annual meeting on Ultrafine Grained Materials*, edited by R.S. Mishra, S.L. Semiatin, C. Suryanarayana, N.N. Thadhani and T.C. Lowe, pp. 73-87, March 12-16, 2000, Nashville, Tennessee.
12. J. He, M. Ice, and E. J. Lavernia, "Bond Strength and Fracture Behavior of Nanostructured NiCr/CrC coatings," *Proceedings of 1999 TMS Fall meeting*, November 1-9, 1999, Cincinnati, Ohio.
13. J. He, M. Ice, and E. J. Lavernia, "Precipitation Phenomenon in Nanostructured NiCr/CrC coatings," *Proceedings of 1999 TMS Fall meeting*, November 1-9, 1999, Cincinnati, Ohio.
14. J. He, M. Ice, M. Peters and E. J. Lavernia, "Influence of fuel-chemistry, fuel-oxygen ratios, and particle size on near nanostructured WC-18% Co coatings," *Proceedings of Fifth International Conference on Nanostructured Materials (NANO 2000)*, August 20-25, 2000, Sendai, Japan.

Invited Lectures and Seminars:

1. E.J. Lavernia, M. L. Lau, and H.G. Jiang, "Thermal spray processing of nanocrystalline materials", *Proceedings of the NATO Advanced Study Institute on Nanostructures Materials: Science and Technology*, G.M. Chow and N.J. Noskova, eds., pp. 283-302, 1998, August 10-20, 1997, St. Petersburg, Russia.
2. "Synthesis of Nanostructured Engineering Coatings by High Velocity Oxygen Fuel (HVOF) Thermal Spraying", lecture presented at *ASM International Materials Solutions conference*, Rosemont, IL, October 12-15, 1998.
3. "Fundamentals of HVOF Thermal Spraying of Ultra-Hard Nanocrystalline Coatings", lecture presented at *The 43rd Annual Conference on Magnetism & Magnetic Materials*, Miami, FL, November 9-12, 1998.
4. "HVOF Thermal Spraying of Nanocomposite Coatings", lecture presented at *Nanocomposite Materials: Design and Applications*, Anchorage, AL, March 28-April 2, 1999.
5. "Thermal Spraying of Nanocrystalline Materials", lecture presented at *44th Sagamore Conference on Nanostructured Materials*, sponsored by US-Army Research Office, Easton, MD, August 23-26, 1999.
6. "Properties and Synthesis of Nanostructured Systems" lecture presented at the Symposium entitled: *Ultra fine-grained Materials*, TMS Annual Meeting, Nashville, TN, and March 2000.
7. "Synthesis of Nanocomposites Coatings" lecture presented at the Symposium entitled: *Surface Engineering in Materials Science*, TMS Annual Meeting, Nashville, TN, March 2000.
8. "Thermal Spraying of Nanocrystalline Materials: Fundamental Issues," *Iketani Foundation International Meeting on Frontiers in Materials*, June 30, 2000, Ritsumeika, Japan.
9. "Science and Application of Nanostructured Coatings," *NanoMaterials Workshop*, CNRS-NSF, France-USA-Canada, Montreal Canada, October 24, 2000.
10. "Mathematical Modeling of HVOF Spraying of Nanostructured Materials: An Overview," *2000 ASME meeting*, Orlando, Florida, November 7, 2000.

2. Scientific Personnel

Dr. Jianhong He, Ph.D
Dr. Honggang Jiang, Ph.D
Dr. Victoria .L. Tellkamp, Ph.D
Dr. Maggy L . Lau, Ph.D
Dr. Degang Chen, Ph.D
Dr. Leonard Ajdelsztajn, Ph.D
Mr. Michael Ice, MS
Mr. Mike Moon, Laboratory Technician (no cost)
Mr. Darryl Mack, Laboratory Technician (no cost)

3. Scientific Progress and Accomplishments

The objectives of this research program were to synthesize and characterize nanostructured thermal spraying coatings. (1) To synthesize nanostructured powders for fabrication of nanostructured thermal spraying coatings; (2) To develop the spray technologies to synthesize nanostructured coatings using nanostructured powders; (3) To utilize advances in process diagnostics and modeling to develop computer-assisted thermal spraying coatings; and (4) To characterize nanostructured materials—powder as well as coatings—for structure, composition, properties and performance.

The research work involves the following four aspects: (1) Synthesis and characterization of diverse nanostructured feedstock powders, i.e. WC-Co, Cr_3C_2-NiCr, Ni, Inconel 625, and Cu-Al powders, using mechanical milling in different media, such as liquid nitrogen, Hexane and methanol; (2) Thermal spray processing for nanostructured coatings. Nanostructured powders were thermally sprayed, as well as conventional ones for comparison purpose using an HVOF facility equipped with in-flight powder diagnostics system. Combined with modeling results, the behavior of powders during spraying was investigated; (3) Characterization of the nanostructured coatings using microhardness, Nanoidentor, SEM, X-ray diffraction, and TEM, so that hardness, wear-resistance, and microstructures can be investigated. On the basis of the feedback of the physical properties of the coatings, the spraying parameters are modified and optimum spraying conditions can be reached for an individual nanostructured powder; and (4) Development of thermal treatment techniques to further improve physical performance of nanostructured coatings. This final report covers the progress made during the period from October 01, 1999 to October 31, 2002. The primary accomplishments are briefly summarized as follows.

3.1 Synthesis of diversified nanostructured feedstock powders.

Preparation of nanostructured feedstock powders is the first step for synthesis of nanostructured coatings. Mechanical milling is used to produce large quantities of nanostructured powders of varying compositions for possible commercial use. Under this program, nanostructured WC-Co, Cr_3C_2-NiCr, Ni, Inconel 625, and Cu-Al powder systems have been successfully synthesized. It is important for nanostructured powder processing to identify powder characteristics, such as particle size, powder morphology, grain size, phase constituents and deformation faults as a function of milling parameters, thus the

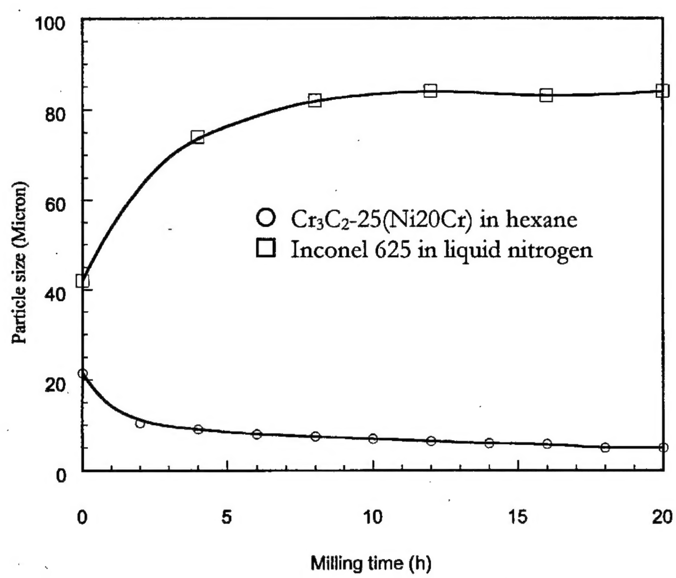
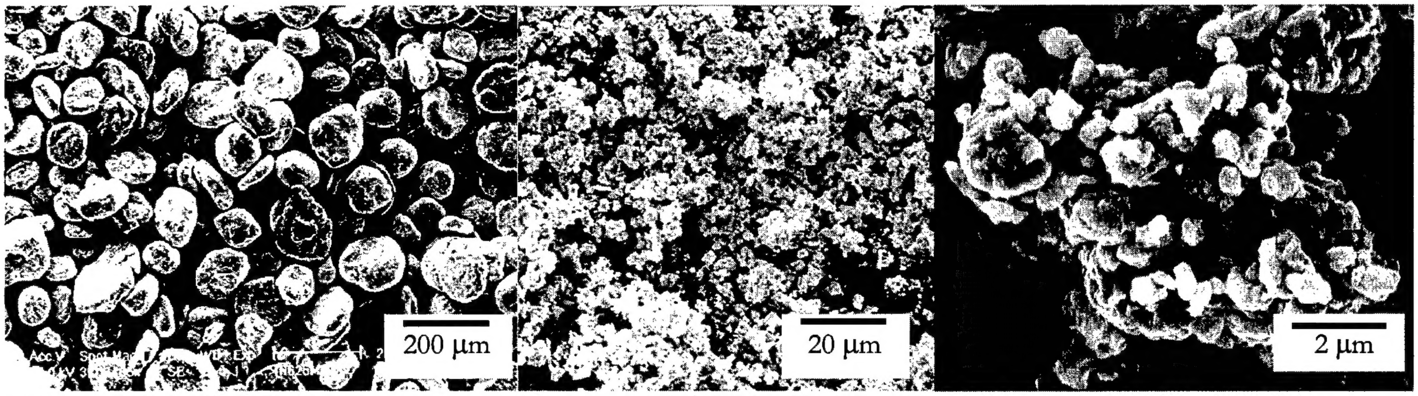


Fig. 1 Dependence of average particle size of Cr_3C_2-25 (Ni20Cr) powder and Inconel 625 superalloy powder on milling time.

dependence of powder characteristics on milling time has been established for each powder system. Figure 1 reveals the dependence of the average particle size of two representative powder systems, ductile single-phase powder and brittle composite powder on milling time. In Figure 1, Cr_3C_2-25 (Ni20Cr) powder is milled in hexane [$H_3C(CH_2)_4CH_3$], and Inconel 625 superalloy powder is milled in liquid nitrogen. As milling time increases, the average particle size of Cr_3C_2-25 (Ni20Cr) powder decreases and approaches a relatively constant value of 5 μm, while that of Inconel 625 increases and approaches a constant value of 84 μm. The commonality of the average particle size of the two powders is that a drastic change occurs within the first four hours of milling, and subsequently stabilizes as milling time increases. The fact that the average particle size changes as milling time increases and approaches a constant value is an indication of fracture and cold welding occurring during milling. Regardless of the initial morphology of as-received powders, milling causes a drastic change in morphology of the powders that undergo severe plastic deformation during milling. Figure 2 reveals the morphology of milled Inconel 625 powder and milled Cr_3C_2-25 (Ni20Cr) powder. The boundaries of milled Inconel 625 powder particles are well defined,

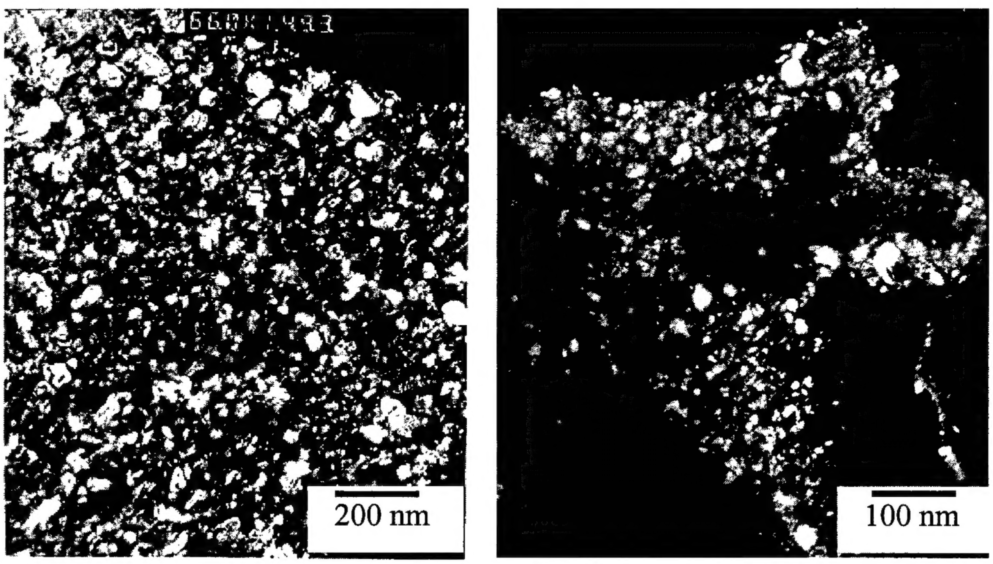
whereas the boundaries of milled composite powders consisting of a brittle phase constituent and a ductile binder constituent, such as Cr_3C_2-NiCr and WC-Co systems, are not clear and powder particles are loosely agglomerated.



(a) Inconel 625 milled for 20 h; (b) Cr_3C_2-25 (Ni20Cr) milled for 20h; (c) Magnification of (b).

Fig.2 Morphology of milled Cr3C2-25 (Ni20Cr) powder and Inconel 625 superalloy powder.

X-ray diffraction and TEM measurement indicates that synthesized powders have grain size in nanometer order. Figure 3 exhibits TEM images of milled Inconel 625 superalloy powder and Cr_3C_2-25 (Ni20Cr) powder. Average grain size for milled Inconel 625 superalloy powder and Cr_3C_2-25 (Ni20Cr) powder are 30 and 15 nm, respectively.



(a) Milled Inconel 625 powder ; (b) Milled Cr_3C_2-25 (Ni20Cr) powder.

Fig. 3 TEM dark field images of Inconel 625 superalloy powder and Cr_3C_2-25 (Ni20Cr) powder.

The presence of high density of deformed faults, such as dislocations and deformation twins, was observed by TEM. Moreover, deformation twins are discovered in materials having high stacking fault energy, i.e. Ni and Al, in which deformation twins had never been reported by others. A twinning mechanism is proposed to be that local lattice distortion in milled powders assisted formation of twins in materials having stacking fault energy. Evolution of microstructure during mechanical milling was carefully investigated and results indicated that coarse grains are elongated, as like as microstructure observed in the material experienced conventional rolling processing, at the initial stage of milling, and then the elongated grains are fractured into fragments- equiaxed nano-size grains.

3.2 Thermal spraying for nanostructured coatings

HVOF is characterized by its high particle velocity and low thermal energy when compared to plasma spraying. Therefore, the coatings developed under this program are synthesized using HVOF thermal spray technique. Utilizing process diagnostics equipment, thermodynamic characteristics of feedstock powders during flight and impingement were experimentally investigated, thus computer simulation of HVOF process can be carried out. Influence of particle size, fuel chemistry and fuel-oxygen ratio on HVOF process has been also systematically studied, and results for near nanostructured WC-18% Co coating are shown in Table 1. From Table 1, it can be seen that powder characteristics and spraying parameters significantly

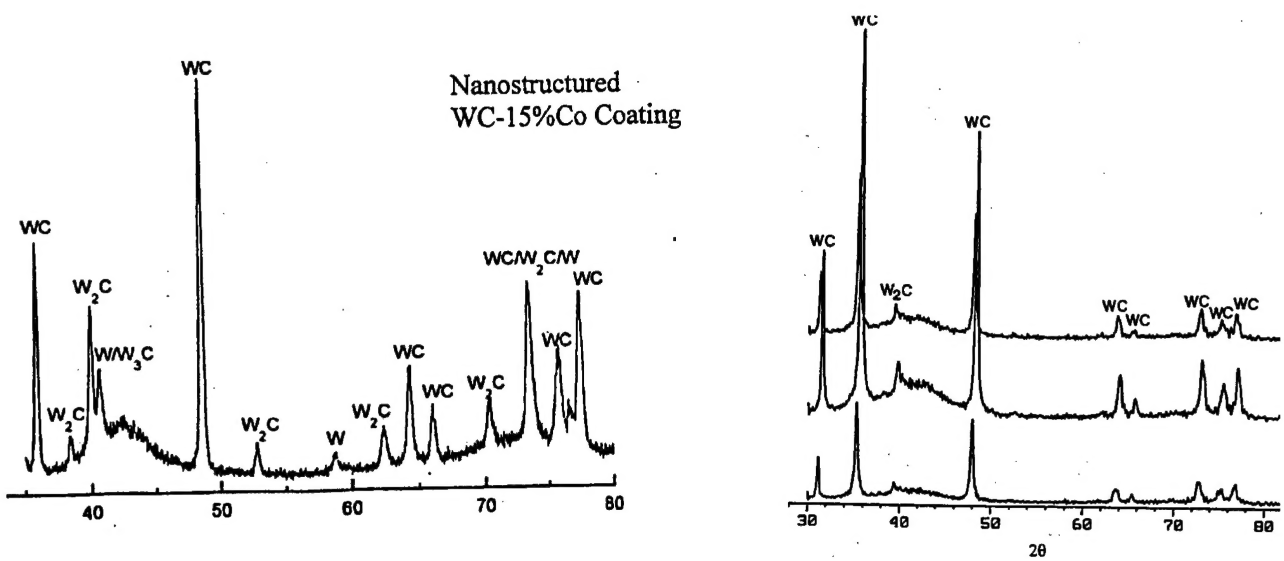
affect thermodynamic characteristics, subsequently mechanical properties of coatings. On the basis of experimental and molding studies, thermal spraying process for nanostructured feedstock powders has been optimized. Consequently, nanostructured coatings with improved performances have been synthesized.

WC-Co system coatings have been widely used in applications required wear resistances, however, decomposition of WC into W_2C and W_3C degrades mechanical properties of nanostructured WC-Co coatings. Figure 4 compares phase constituents of nanostructured WC-Co coating synthesized under this program by an optimized HVOF process with that appeared in a literature [D. A. Stewart, P. H. Shipway, and D. G. McCartney, *Wear*, 1999, 225-229, p 789.] Although W_2C and W_3C brittle phases are potentially formed with nanostructured feedstock powder, an optimized combination of spraying parameters with powder characteristics is able to synthesize nanostructured coatings with very low amount of W_2C phase and high performance. The result for the sample MP32 in Table 1 and 2 is a good example demonstrating that high performance of coatings is achieved under an optimized combination of spraying parameters with powder characteristics.

Table 1. Influence of fuel-chemistry, fuel-oxygen ratios, and agglomerate size on near nanostructured WC-18% Co coatings

Code	Particle Size (μm)	Fuel*	Fuel/O_2	T (K)	W_2C (vol.%)	Porosity (vol.%)	HV_{1kg} (kg/mm^2)	Sliding Wear Rate (x10^{-6} mm^3/Nm)	Abrasive Wear Rate (x10^{-2} mm^3/Nm)
SH62	20	H	2.8	1870	8.7	11	1000	028	1.50
MH45	32	H	2.0	1520	1.6	25	N/A	N/A	N/A
MH62	32	H	2.8	1810	3.8	12	830	0.32	1.20
MH75	32	H	3.5	1840	4.7	10	1020	0.38	1.10
LH62	39	H	2.8	1690	2.9	12	740	0.30	1.00
MP32	32	P	0.24	2130	3.8	2	1240	0.19	0.78
MP40	32	P	0.30	2290	6.7	2	1160	0.20	0.90
MP48	32	P	0.37	2220	5.7	2	1120	0.36	1.10

* H is hydrogen, and P stands for propylene.



(a) Nanostructured WC-15% Co coating with high amount of W_2C and W_3C phases by D. A. Stewart et al;

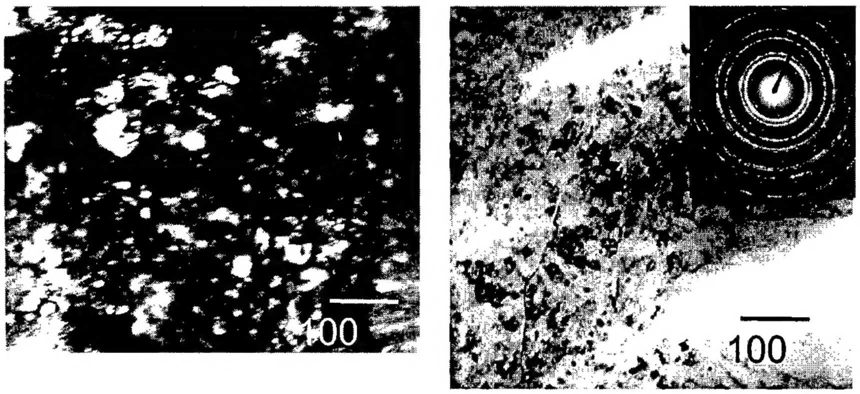
(b) Nanostructured WC-18% Co coating with low amount of non WC carbide phase under this program.

Fig. 4. XRD spectra for nanostructured WC-Co coatings

3.3 Characterization of the nanostructured coatings

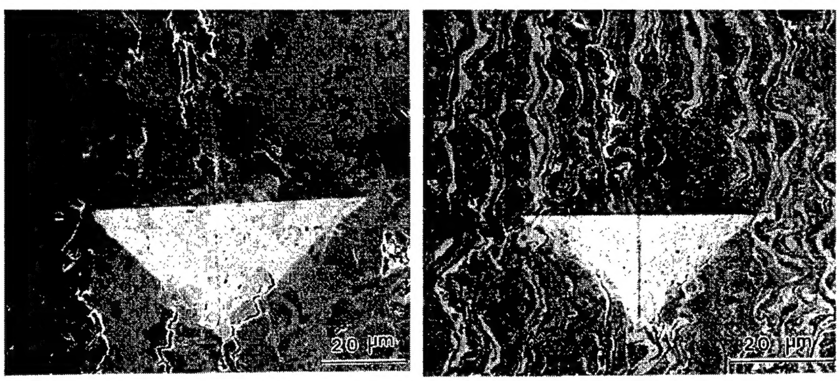
Microstructures of synthesized coatings were examined by using SEM and TEM to confirm the preservation of nanostructures of nanostructured feedstock powders in the coatings. Results shown in Figure 5 indicated that synthesized coatings still have nanostructures.

Mechanical properties of nanostructured coatings have been significantly improved. For example, the average microhardness of the nanostructured Cr_3C_2-25(Ni20Cr) coating increases from a value of 846 for the conventional Cr_3C_2-25(Ni20Cr) coating to 1020 HV_{300} for the nanostructured coating. Hence the nanostructured coating exhibits a 20.5 % increase in microhardness and as compared with the corresponding conventional coating. A 28% increase in wear-resistance with nanostructured coating is also measured. In addition to improved hardness and wear-resistance, the apparent toughness of nanostrutured coatings also increased. Figure 6 shows the indentation on Cr_3C_2-25(Ni20Cr) coatings under a load of 1000 gram. Many cracks caused by an indentation along the phase interface of carbide phase with metal matrix phase were observed in the conventional coating, and only a few cracks were found in the nanostructured coating. This indicates that nanostructured coatings have higher apparent toughness than conventional coatings.



(a) Nanostructured Cr_3C_2 Coating; (b) Nanostructured Ni coating.

Fig. 5 TEM images of coatings synthesized using nanostructured feedstock powder, indicating the presence of nanostructure in coatings.



(a) Conventional coating; (b) Nanostructured coating;

Fig. 6 Indentation crackings on Cr_3C_2-25(Ni20Cr) coatings under a load of 1000 gram

3.4. Development of thermal treatment techniques for nanostructured coatings

Thermal sprayed nanostructured coatings have non-equilibrium microstructure, which results in subsequent precipitation during aging, and thus provide a potential approach to further improve physical performances of nanostructured coatings.

For example, Figure 7 depicts influence of thermal exposure on hardness of Cr_3C_2-25(Ni20Cr) coatings. Microhardness of the conventional coating only increased slightly with increased exposure to all temperature ranges, while that of the nanostructured coating drastically increased from 1020 to 1240 HV_{300} in the temperature range 700 to 900 K, and then approached a constant value.

TEM examination shown in Figure 8 indicates that during thermal exposure, high density of ultrafine particles are precipitated in the nanostructured matrix. Figure 8 reveals spherically shaped precipitates in the nanostructured coating treated at 1073 K that were likely to have formed by nucleation and growth in the matrix. In addition to original carbide particles, some very fine precipitates were observed. The average size of the original carbide particles increased from 24 nm in the as-sprayed

nanostructured coating to 39 nm in the nanostructured coating exposed at 1073 K, whereas the precipitates had an average size of 8.3 nm, and precipitating hardening not only compensate the loss in hardness caused by slight grain growth of original carbide, but also provide extra hardness, subsequent wear-resistance for nanostructured coatings

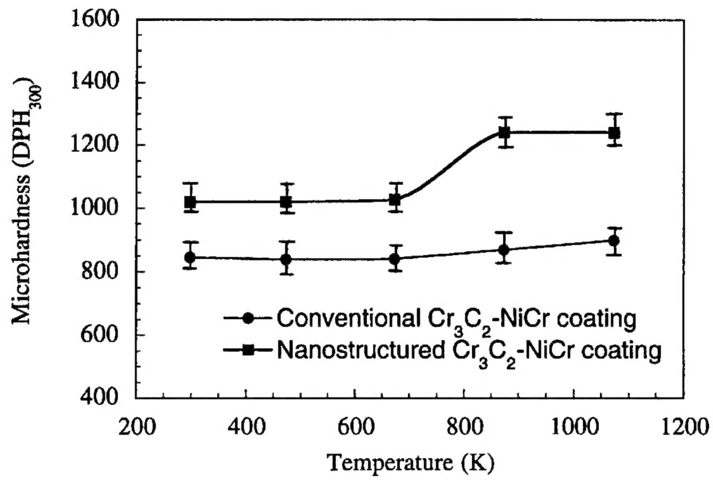


Fig. 7 Variation of microhardness of Cr_3C_2-25(Ni20Cr) coatings with heat treatment temperature.

Fig. 8. TEM image of nanostructured Cr_3C_2-25(Ni20Cr) coatings exposed at 1073 K for 8h, "P" indicates precipitates, and "O" indicates matrix grains.

4. Technology Transfer

Potential applications of thermal spraying coatings span the entire spectrum of technology, from thermal barrier coatings for turbine blades to wear resistant rotating parts. For example, there are approximately 1500 weld overlays in a single ship. The anticipated life cycle of these welds could be significantly extended if a nanostructured coating, with the associated improvements in hardness and wear characteristics, could be used. Moreover, it has been estimated that a significant proportion of the valve stems that fail in ships are due to steam erosion. The improved wear properties of nanostructured coatings are ideally suited for this particular application. This and other examples suggest that the applications of thermal sprayed nanostructured coatings can extend to a broad range of industries, including Navy, aerospace and automotive, and cover a wide spectrum of materials that could be used to fabricate diverse components. The potential economic impact is several billions of dollars per year.